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Diurnal and Seasonal Patterns of Particulate Sulfur and Sulfuric Acid in St. Louis, July 1977-June 1978

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DIURNAL AND SEASONAL PATTERNS OF PARTICULATE SULFUR AND SULFURIC ACID IN ST. LOUIS, JULY 1977–JUNE 1978

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Abstract—Continuous measurements of particulate sulfur and sulfuric acid were taken in St. Louis over a one year period using the *in-situ* thermal analysis-flame photometric method. These measurements were used to calculate average diurnal patterns for each quarter of the year, and also the seasonal pattern for one year. Enhanced formation of particulate sulfur during the daytime hours of spring and summer is indicated by an afternoon concentration increase of about 20%. The diurnal patterns of aerosol acidity and charge (a bulk measure of 0.01–0.1 μm particles) also support this notion. Particulate sulfur and light scattering coefficient exhibited moderate seasonal variation. For the third quarter, particulate sulfur concentration was higher than the annual mean by 40% and light scattering coefficient was higher by 25%.

1. INTRODUCTION

The principal features of the particulate sulfuric acid/sulfate air pollution problem are now understood in at least a coarse way. Sulfur transmission through the atmosphere, through meteorological transport and various transformations can be modeled in a realistic, if not accurate sense. The average spatial distribution of particulate sulfur throughout the eastern United States is reasonably well known (e.g. Altshuller, 1976; Hidy *et al.*, 1978; Husar and Patterson, 1980). A detailed description of the temporal behavior of particulate sulfur is lacking, because of the great number and detail of measurements that would be required. The temporal behavior would be expected to vary substantially with location, depending on the source–receptor configuration and meteorology. Both the temporal and spatial features of particulate sulfuric acid pollution are poorly known because the measurement techniques for this compound have not been as well developed as those for sulfate and total particulate sulfur (Newman, 1978). A detailed description of the spatial and temporal characteristics of sulfuric acid and ammonium sulfate salts would be useful in order to characterize the air quality for estimation of effects, and for providing supporting information for studies concerning source–receptor relationships.

Measurements taken in St. Louis, and in other parts of the northeastern United States have indicated some general features of the temporal behavior. In St. Louis, the mean absolute rate of change of particulate sulfur concentration on the basis of hourly measurements over a one-year period was $0.5\,\mu g\,m^{-3}\,h^{-1}$, which compares to a mean concentration of $2.5\,\mu g\,m^{-3}$ (Cobourn, 1979). Thus, short term variation was moderate. Several investigations of longer term behavior have shown that variation of daily average sulfate concentration is characterized by excursions or upswings which occur on a cycle of about 4–7 days (Cobourn *et al.*, 1980; Lavery *et al.*, 1980; Lippman *et al.*, 1979; Loo *et al.*, 1978). This often observed pattern is a consequence of the fact that sulfate pollution extends to synoptic scales, and is therefore associated with the movement of synoptic weather systems. Observations of the seasonal patterns of particulate sulfur in the eastern U.S. have generally indicated a summer increase of about 30–50% over the annual average (Husar and Patterson, 1980; Hidy *et al.*, 1978; Hitchcock, 1977). Analysis of particulate data for the year 1976 from the EPA Regional Air Monitoring System (RAMS) by Trijonis *et al.* (1980) revealed this same pattern for both urban and rural sites near St. Louis. Studies of the diurnal pattern of particulate sulfur are not wholly consistent, because local source and terrain effects come into play. A pattern of afternoon increase in sulfate concentration has sometimes been observed (Wolff *et al.*, 1980; Stevens *et al.*, 1980; Winchester, 1980). However, analysis of the 1976 RAMS data by Trijonis *et al.* (1980) revealed no significant diurnal variation of particulate sulfur.

Measurements of sulfuric acid and particulate sulfur were carried out in St. Louis over a one-year period (July 1977–June 1978) using an *in-situ* thermal analysis-flame photometric detector (TA-FPD) monitor developed at Washington University (Cobourn *et al.*, 1978). The TA-FPD monitor produces a continuous electrical signal which is recorded and later processed to provide 15 min time resolution data. The detail and extent of these data have made possible the close examination of at least two sulfuric acid episodes (Cobourn *et al.*, 1980), and the analysis of diurnal and seasonal patterns of sulfate and sulfuric acid provide information concerning the atmospheric processes which produced the pollutants, i.e. transport, transformation and removal.

2. MEASUREMENT AND ANALYSIS TECHNIQUES

The aerosol measurement system is based on the principle of *in-situ* thermal analysis, in which continuous monitoring instruments measure ambient aerosol which has been pretreated by a temperature programmed heater tube (Cobourn *et al.*, 1978). Three continuous instruments are used: a Meloy SA-285 FPD sulfur analyzer (Lucero and Paljug, 1974), a nephelometer (Charlson *et al.*, 1969) and a charger (Husar *et al.*, 1976). The programmed heater ramps the temperature to 300° C at the rate of 30° C min^{-1} once every 15 min. At 300° C, 80–90% of the ambient aerosol and nearly 100% of the sulfate compounds are volatilized by the heater. From each instrument comes a temperature dependent volatilization curve called a thermogram.

The FPD particulate sulfur monitor is a relatively new technique whereby sulfur is continuously measured from the 394 ± 5 nm wavelength light emissions produced by excited sulfur molecules in a hydrogen flame. The instrument is made specific to particulate sulfur by scrubbing SO_2 with a diffusion tube denuder (Durham *et al.*, 1978) which precedes the inlet to the FPD burner. The instrument has a detection limit of about 1 μg m^{-3}, which is below the ambient particulate sulfur concentration in St. Louis 80% of the time (Cobourn, 1979). Results of a recent EPA sponsored field intercomparison study of various types of particulate sulfur measurement systems demonstrated that FPD monitors can measure hourly average concentrations to within ± 5% if properly calibrated and zeroed (Camp *et al.*, 1981). The percentage accuracy depends on the concentration, though, for at the detection limit of 1 μg m^{-3}, the percentage accuracy is no better than ± 50%.

The sulfur thermogram indicates the amount of sulfuric acid present, since sulfuric acid volatilizes mostly below 175° C in this system, and the ammonium salt compounds [$(NH_4)_2SO_4$, NH_4HSO_4, $(NH_4)_3H(SO_4)_2$] volatilize mostly above 175° C. The analysis is only semi-quantitative, since the response to mixtures of acid and salt compounds depends on the type of aerosol mixture; i.e. whether a homogeneous aerosol with solution mixtures in the particles (internal mixture), or a heterogeneous aerosol with pure solutions in the particles (external mixture) (Cobourn *et al.*, 1980). The light scattering and charger thermograms indicate the chemical composition of those particular aerosol components in a qualitative way, by describing the volatility.

These measurements were continuously made on the St. Louis ambient aerosol, and recorded on magnetic tape, for a one-year time period. The FPD analyzer and nephelometer were periodically calibrated, using a permeation tube calibration system for the FPD, and a freon-12 scattering standard for the nephelometer. The calibration information was factored into the data during the computer post-processing. During later stages of computer processing, various analyses of the data were performed to determine statistical parameters, diurnal patterns, seasonal patterns, etc.

The thermal analysis measurements have been parameterized by dividing each aerosol measurement into a number of components according to volatility. For example, light scattering coefficient is divided into three components as follows:

$$b_{scat} = b_I + b_{II} + b_{res} \quad (1)$$

$$b_I = b_{scat}(50^\circ\text{C}) - b_{scat}(175^\circ\text{C}) \quad (2)$$

$$b_{II} = b_{scat}(175^\circ\text{C}) - b_{scat}(300^\circ\text{C}). \quad (3)$$

The residual light scattering coefficient b_{res} can be further subdivided into a component due to non-volatile particles and a component due to Rayleigh air scattering. Particulate sulfur and charge are classified in the same way, resulting in the terms S_I, S_{II}, C_I, C_{II}, etc. The highly volatile particulate sulfur S_I is associated with sulfuric acid, and the moderately volatile component S_{II} is associated with the ammonium salt compounds. The volatile components of light scattering coefficient and charge are less specific indicators of chemical composition, but from knowledge of the composition of pollution aerosols (e.g. Lewis and Macias, 1980), it may be reasoned that sulfates, nitrates, organic compounds and water make up most of the volatile material.

The distribution of material between the various volatile components depends on the aerosol chemical composition. Therefore, one useful index of aerosol chemical composition is the fraction of volatile material in the highly volatile class. The sulfur volatility index, or acidity index, is defined as follows:

$$F_s = S_I/(S_I + S_{II}). \quad (4)$$

At particulate sulfur concentrations near the detection limit of 1 μg m^{-3} this index cannot be measured very accurately, since it requires resolving S_p into parts (S_I and S_{II}). The accuracy improves rapidly with increasing S_p concentration, however, because the FPD signal is approximately proportional to the square of the sulfur concentration. At particulate sulfur levels in the range $1\ \mu\text{g m}^{-3} < S_p < 2\ \mu\text{g m}^{-3}$, the component parts of S_p can be resolved to about $\pm 0.1\ \mu$g m^{-3}. At levels above $S_p = 2\ \mu$g m^{-3} the uncertainty in the components S_I and S_{II} is probably about double that of S_p, or about ± 10%.

Other volatility indices based on the nephelometer and charger thermograms (F_b and F_c) are defined in an analogous manner. These aerosol parameters, plus some additional parameters derived from these, have been analyzed in terms of averages of various time scales, the annual patterns, and the average diurnal patterns. The average diurnal patterns were calculated for each quarter of the year, based on 1-h averages of the data.

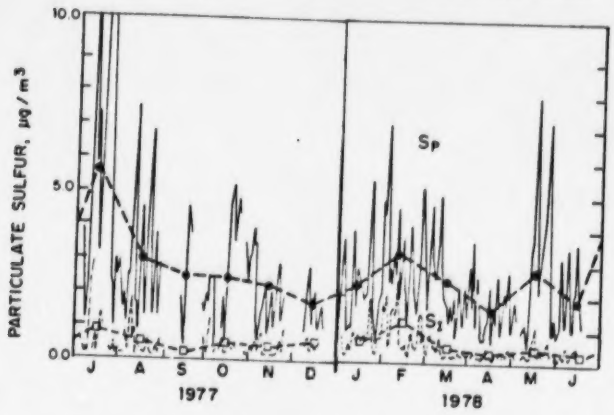

Fig. 1. Time series of particulate sulfur and acidic sulfur, daily and monthly averages, for one year.

3. SEASONAL BEHAVIOR

3.1. *Daily and monthly averages*

A plot of the monthly average particulate sulfur concentration for the July 1977–June 1978 period (Fig. 1) shows that the highest monthly average concentration was in July ($5.5\,\mu g\,m^{-3}$), and the lowest monthly average was in April ($1.7\,\mu g\,m^{-3}$). The third quarter average of $3.5\,\mu g\,m^{-3}$ was 40% higher than the yearly average, consistent with other observations of a summer increase in other parts of the eastern United States (eg. Husar and Patterson, 1980; Trijonis *et al.*, 1980; Hidy *et al.*, 1978; Hitchcock, 1977). The monthly average acidic particulate sulfur (S_I) concentration was generally around $0.5\,\mu g\,m^{-3}$.

The daily average particulate sulfur concentrations (Fig. 1) exhibited excursions of typically 4–7 days length, reflecting the influence of the synoptic scale transport. The daily average light scattering coefficient exhibited very similar temporal behavior (Fig. 2), as well as a close correlation ($r = 0.86$) with particulate sulfur. In these data there appears to be a background level of particulate sulfur, below which the daily average concentration seldom went. This level was at about $1\,\mu g\text{–}S\,m^{-3}$, or slightly lower. Similarly, there was an apparent background level of light scattering coefficient which was roughly $0.5\,10^{-4}\,m^{-1}$, about 150% above the level of scattering by air molecules.

The acidity index (F_a) and volatility index (F_b) each showed a marked seasonal variation (Fig. 3); both the acidity and volatility tended to be higher during the colder months of the year (quarters one and four). There was also significant day-to-day variation in the indices, again on a temporal scale of about 4–7 days. The overall patterns of these indices suggests that there was a general seasonal variation in the chemical composition of the aerosol; i.e. the aerosol tended to contain a greater proportion of acidic compounds and highly volatile compounds during the colder months.

There are several possible reasons for these effects. First, ammonia emissions and atmospheric concen-

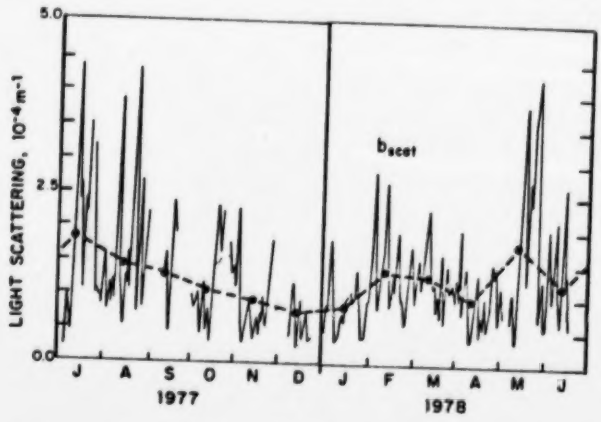

Fig. 2. Time series of light scattering coefficient, daily and monthly averages, for one year.

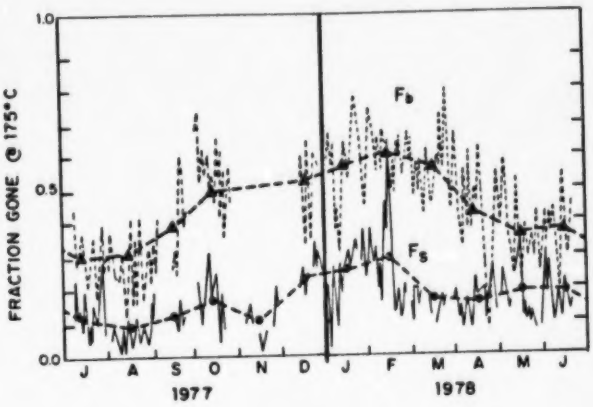

Fig. 3. Time series of acidity index and volatility index, daily and monthly averages, for one year.

trations are thought to be an order of magnitude lower during the wintertime as compared to summer (National Research Council, 1979), while particulate sulfur concentrations are reduced by only about 50% in wintertime. The reduced neutralizing capacity of the atmosphere in winter should thus lead to more acidic aerosols. Secondly, the average transport wind is somewhat greater in winter than in summer (Holzworth, 1967), which means that, on average, there would be a shorter residence time from source to receptor within the major sulfur emissions region of the eastern U.S. The average winter aerosol would thus tend to be less aged and less likely to have been neutralized. The lowered winter mixing height probably also played a role in changing the chemical composition, by increasing the concentration of local emissions. Thus, freshly formed sulfuric acid, produced from local SO_2 emissions, and organic and elemental carbon aerosol, produced from automobiles, home heating and industrial processes, would each tend to contribute a greater proportion of material to the urban aerosol.

The charge to light scattering ratio is an indicator of the physical composition of the aerosol, since the charger measures primarily the particles less than 0.1 μm in diameter. There was a definite seasonal pattern in this parameter, with the winter values being relatively high, indicating a relatively greater amount of small (< 0.1 μm) particles. It is difficult to say how much this effect reflects a physical change in the regional aerosol transported into the urban area, and how much is caused by local emissions of small particles into the lowered winter mixing layer. Seasonal shifts in chemical and physical composition have also been observed by other researchers (Kadowaki, 1976; Hitchcock, 1977). As these shifts are indicative of fundamental changes in the source-receptor relationships, a better understanding of their causes could be important for control of haze type aerosol pollution.

3.2. *Frequency distribution and averaging time*

The frequency distribution and the averaging time are two aspects of air pollution measurement which are relevant to the problem of relating atmospheric concentrations to environmental effects. The frequency distribution depends on the averaging time, becoming less dispersed as the averaging time of the measurements is increased. In some cases, one may desire a frequency distribution of values to describe the concentration effect relationship. This would be especially true of short-term effects, where the peaks, valleys, and variability in concentration are important.

In the case of sulfate pollution, the concentration variability in many locations is largely associated with the movement of synoptic scale air masses. As a result, data sets of daily average concentration are generally adequate to characterize the full variability in concentration over a period of several weeks or more. In a statistical analysis of the St. Louis data, the spread of the quarterly frequency distributions decreased only slightly as the data averaging time increased from 1 to 24 h (Fig. 5). Notice that as the averaging time was again increased by the same factor, from 1 to 24 days, the frequency distribution was much compressed. A glance at the time-series plot of daily average particulate sulfur concentration (Fig. 1) reveals why some of the peaks and valleys in the data began to be smeared out as the averaging time was increased beyond one day.

4. DIURNAL BEHAVIOR

The average diurnal patterns of 18 measured and derived pollutant parameters were calculated for each quarter of the year, to allow possible seasonal effects to show up. The parameters have been plotted in six groupings for each quarter (Figs 6–9).

4.1. *Particulate sulfur*

Particulate sulfur (S_p) and acidic sulfur (S_I) each

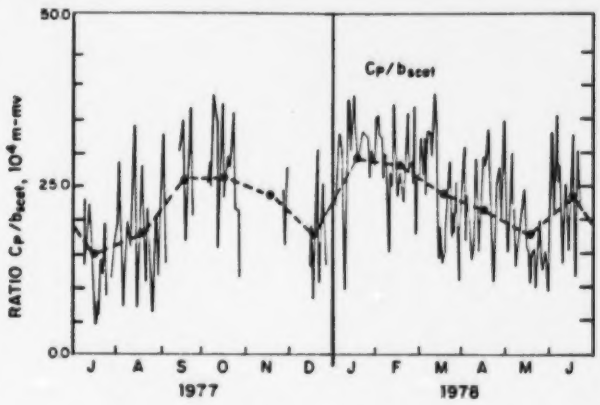

Fig. 4. Time series of the ratio C_p/b_{scat}, daily and monthly averages, for one year.

exhibited a significant diurnal variation during the spring and summer quarters (quarters two and three), but not during the other quarters. During these two quarters particulate sulfur tended to increase during the daytime and decline at night. The increase from night to day represents about 20% of the quarterly average concentration. This pattern would be consistent with the notions of enhanced sulfate formation during the daytime (Gillani *et al.*, 1978), and an average residence time for sulfate of 5–7 days (Rodhe, 1978). Enhanced daytime formation has been observed in plume measurements, and is thought to be due to photochemically induced gas phase reactions and atmospheric mixing (Gillani and Kohli, 1980). A possibly significant mechanism in producing this pattern would be the daytime entrainment of elevated pollutant layers delivered by night-time transport. However, since the opposite effect would also be possible, i.e. entrainment of relatively cleaner air, it seems unlikely that this mechanism would produce any overall diurnal variation. The fact that no diurnal variation occurred during the fall and winter quarters may indicate that there are seasonal shifts in the relative importance of the various sulfate formation mechanisms. If solar radiation does indeed play a key role in sulfate formation, then in the wintertime, when

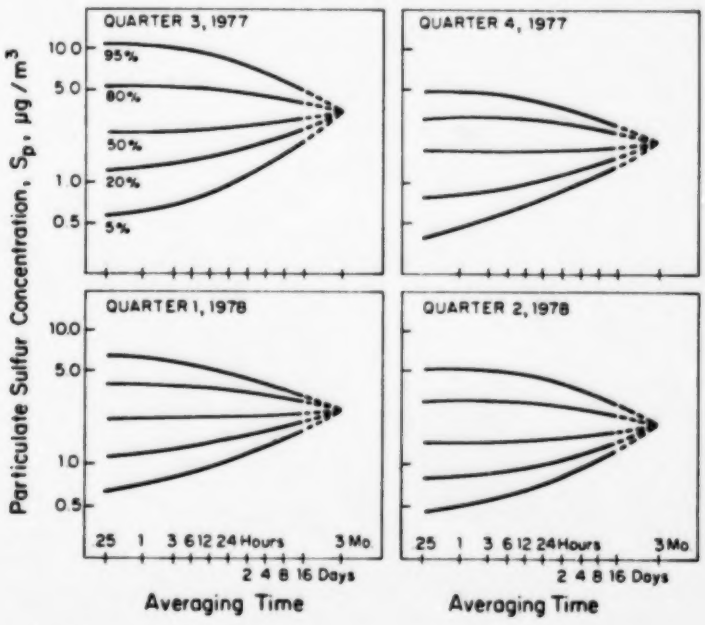

Fig. 5. Frequency distributions of particulate sulfur, vs averaging time, for each quarter of the year.

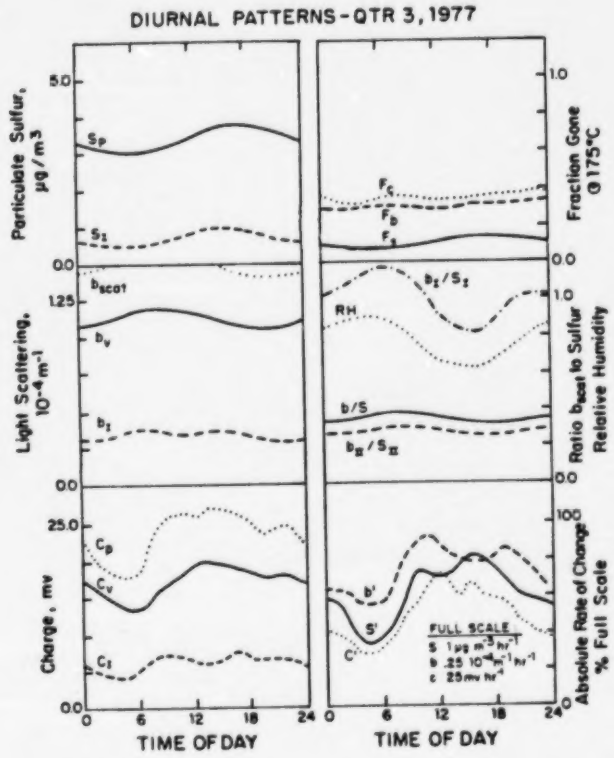

Fig. 6. Average diurnal patterns of aerosol parameters during quarter three, 1977.

there is generally far less solar radiation, its role would be largely diminished. Diurnal patterns of particulate sulfur calculated by Trijonis *et al.* (1980) based on 1976 RAMS data from two urban sites showed no significant diurnal variation. In contrast, our data does show a pattern of a 5–10% afternoon increase when grouped together for a whole year. Data from the following one year period also show this pattern. The apparent discrepancy in results from different years cannot presently be explained; further analysis of our data may help to elucidate the matter.

4.2. *Light scattering coefficient*

The seasonally averaged diurnal patterns of light scattering coefficient did not resemble those of particulate sulfur. This is remarkable, since these two parameters generally correlated very well when unaveraged short term data taken over several days time were compared. For example, during quarter three, the b_{scat} pattern shows a daytime decline rather than an increase. This pattern of afternoon decline is to some extent reflected in three of the four quarters; it may also be seen in the average diurnal pattern of light scattering to particulate sulfur ratio, which also tended to decline during the daytime. One possible means of explanation is the daytime decline in relative humidities; the ambient aerosol would tend to contain less water and scatter less light per unit of sulfur mass. Though our b_{scat} measurements were taken at the 50°C point on the temperature ramp, they are not really "heated" or "dry" b_{scat} measurements. This is because the aerosol does not enter the nephelometer at the heater exit temperature; it actually cools down to room temperature in the tubing along the way. Since the light scattering aerosol contains material other than particulate sulfur, it is also possible that this diurnal pattern is influenced by local emissions such as those from automobiles.

4.3. *Charge*

The charger is a fast response aerosol detector which is highly sensitive to particles of approximately 0.01–0.1 μm in size (Husar *et al.*, 1976). Thus, it provides a bulk measurement of small particles which are usually associated with fresh combustion sources. The diurnal pattern of charge would therefore be expected to reflect the diurnal traffic pattern. In all quarters there was indeed a decline in this indicator from midnight to 6 a.m., then an increase with the onset of morning rush hour traffic. In the diurnal patterns of quarters one and four, there are two peaks, corresponding to the morning and evening rush hours. These morning and evening peaks are not discernable on the plots of quarters two and three, possibly

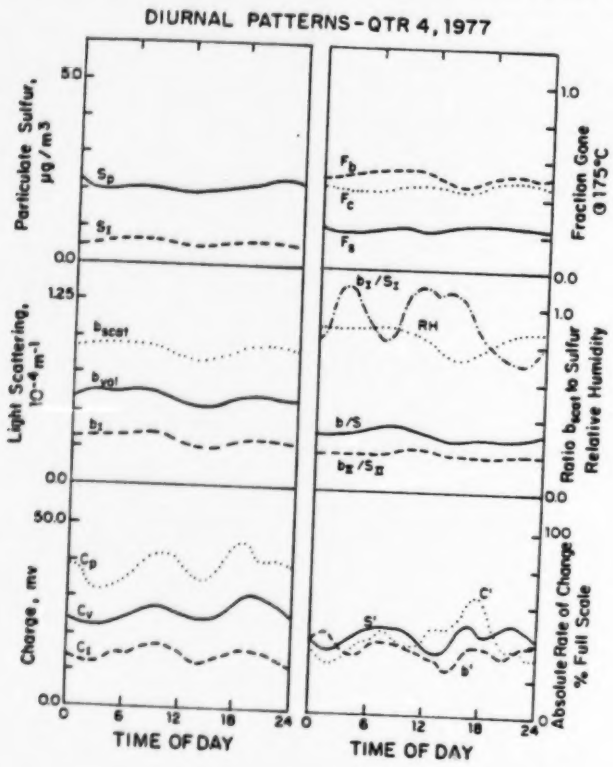

Fig. 7. Average diurnal patterns of aerosol parameters during quarter four, 1977.

because nuclei formation from photochemical production mechanisms created a third peak at midday, obscuring the rush hour effect on the patterns.

4.4. *Acidity index, volatility indices*

These indices of chemical composition generally did not exhibit much diurnal variation, except for the acidity index (F_s) which increased during the afternoon hours of quarter three. This further supports the notion of enhanced aerosol formation during the afternoon hours of the summer quarter, since freshly formed sulfate aerosol would be acidic.

4.5. *Light scattering to particulate sulfur ratio*

The light scattering to particulate sulfur ratio is useful as a rough indicator of the role of particulate sulfur in light scattering (e.g. Waggoner *et al.*, 1976). It is only a rough indicator since the light scattering coefficient is dependent on a number of variables besides mass concentration, including particle size, shape, and refractive index. This ratio does exhibit a diurnal variation in three of four quarters. As previously discussed this variation could possibly be related to the diurnal variation in relative humidity. It may be noted that the ratio b_1/S_1, which applies only to the highly volatile aerosol material which volatilizes below 175°C, generally exhibits the most diurnal variation, and in quarters two and three the pattern is remarkably similar to that of relative humidity.

4.6. *Aerosol rate of change*

The average diurnal pattern of absolute rate of change of aerosol levels indicates when aerosol concentrations tended to change, whether positively or negatively. One might expect that the absolute rate of concentration change would be greatest during the day, when both aerosol formation and vertical transport are more active. During quarters two and three this was the case. During quarter four there was little diurnal variation in this parameter, and during quarter one there was a night-time peak. The difference in the fall and winter patterns may be due to the effect of local sources such as home heating from oil; primary emissions into the nocturnal surface layer could create considerable concentration swings.

Examination of the diurnal patterns of all of these parameters seems to indicate some consistency between quarters two and three, and also some degree of consistency between quarters one and four. This is evident even with the volatility indices, which show practically no diurnal variation, but which are systematically higher during quarters one and four. This dichotomy was probably created by the marked differences in meteorology, photochemistry and emission

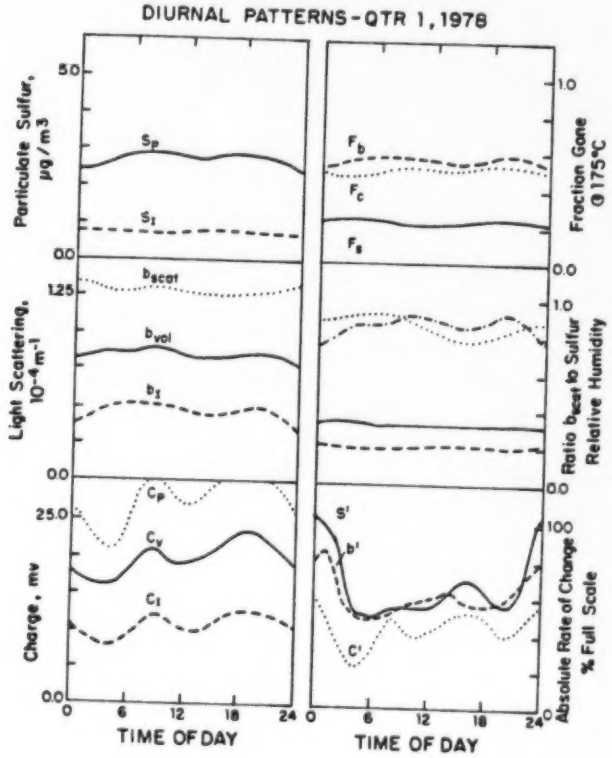

Fig. 8. Average diurnal patterns of aerosol parameters during quarter one, 1978.

source configuration which occur between the warmer and the colder parts of the year.

5. CONCLUSIONS

The temporal behavior of daily concentrations of particulate sulfur over a one year period in St. Louis showed the influence of long range transport and synoptic scale air mass movements by the cyclic upswings in concentration, which typically occur on a 4–7 day time scale. Daily average light scattering coefficient behaved in a similar manner. The seasonal pattern of particulate sulfur concentration exhibited a third quarter increase of about 40% over the annual mean, consistent with other reported measurements in the eastern U.S. This pattern suggests that there may be an increased average aerosol formation rate during the summer; however, without an explicit account of all of the chemical and meteorological processes involved, the nature and causes of this effect are not fully explained.

The volatility and also the acidity of the ambient aerosol tended to be higher during the colder part of the year, indicating a seasonal pattern in aerosol chemical composition. The ratio of charge to light scattering coefficient tended to be higher during the colder months, indicating a seasonal pattern in physical composition. These observed patterns are probably due to differences in transport meteorology between summer and winter, and also seasonal changes in emissions of sulfur oxides and ammonia.

The diurnal pattern of particulate sulfur concentration exhibited an afternoon increase during the spring and summer quarters, while the fall and winter quarters exhibited no significant diurnal variation. These patterns may have arisen because of aerosol formation enhanced by solar radiation and atmospheric mixing. These processes would be much more pronounced during the warmer parts of the year. The acidity index also exhibited slight afternoon increases during the spring and summer quarters, again indicating enhanced aerosol formation during those times.

The diurnal patterns of light scattering coefficient were not similar to those of particulate sulfur. The cause of this difference is not clear, but it may be related to relative humidity, or locally produced, non-sulfur light scattering aerosol material. The average diurnal patterns of charge reflect the diurnal traffic patterns, and in the spring and summer quarters show an additional afternoon peak which may be due to homogeneous nucleation of particles.

Both the seasonal and diurnal patterns would be expected to vary with location. These observations

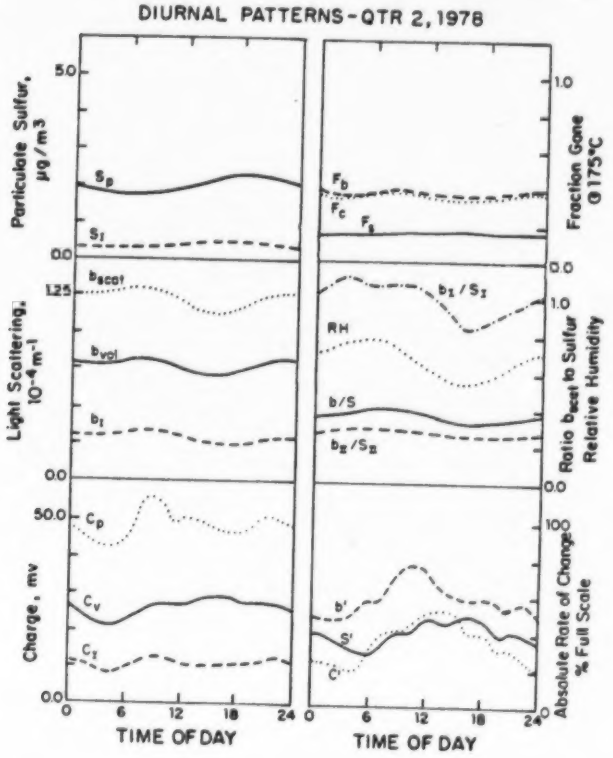

Fig. 9. Average diurnal patterns of aerosol parameters during quarter two, 1978.

may generally hold for many other urban sites in the eastern U.S. where terrain and emission density are roughly similar to those of St. Louis. However, in areas with very strong sources of primary sulfates, with strong terrain effects, or in very remote areas, different patterns would probably be observed.

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REFERENCES

Camp D. C., Stevens R. K., Cobourn W. G., Husar R. B., Collins J. F., Huntzicker J. J., Husar J. D., Jaklevic J. M., McKenzie R. L., Tanner R. L., Tesch J. W. (1981) Intercomparison of concentration results from fine particle sulfur monitors. *Atmospheric Environment* (in press).

Cobourn W. G., Husar R. B. and Husar J. D. (1978) Continuous *in-situ* monitoring of ambient particulate sulfur using flame photometry and thermal analysis. *Atmospheric Environment* **12**, 89–98.

Cobourn W. G. (1979) *In-situ* measurements of sulfuric acid and sulfate aerosol in St. Louis. D.Sc. Dissertation, Washington University, St. Louis, Missouri.

Cobourn W. G., Djukic-Husar J. and Husar R. B. (1980) Monitoring of sulfuric acid episodes in St. Louis, MO. *J. geophys. Res. Oceans Atmos.* **85**, 4487–4494.

Charlson R. J., Ahlquist N. C., Selvidge H. and MacReady P. B., Jr. (1969) Monitoring of atmospheric aerosol parameters with the integrating nephelometer. *J. Air Pollut. Control Ass.* **19**, 937–942.

Durham J. L., Wilson W. E. and Baker B. E. (1978) Application of an SO_2 denuder for continuous measurement of sulfur in submicrometric aerosols. *Atmospheric Environment* **12**, 883–86.

Gillani N. V., Husar R. B., Husar J. D., Patterson D. E. and Wilson W. E. (1978) Project MISTT: kinetics of particulate sulfur formation in a power plant plume out to 300 km. *Atmospheric Environment* **12**, 589–598.

Gillani N. V., Kohli S. and Wilson W. E. (1981) Gas-to-particle conversion of sulfur in power plant plumes: I. Parametrization conversion rate for dry, moderately polluted ambient conditions. *Atmospheric Environment* **15**, 2293–2314.

Hidy G. M., Mueller P. K. and Tong E. Y. (1978) Spatial and temporal distributions of airborne sulfate in parts of the United States. *Atmospheric Environment* **12**, 735–752.

Hitchcock D. R. (1977) Biogenic sulfur sources and air quality in the U.S. Final Report, NSF-RANN No. AEN-7514571, Arthur D. Little, Inc., Cambridge, MA.

Holzworth G. C. (1967) Mixing depths, wind speeds and air pollution potential for selected locations in the United States. *J. Am. met. Ass.* **6**, 1039–1044.

Husar R. B., Macias E. S. and Dannevik W. P. (1976) Measurement of dispersion with a fast response aerosol detector. 3rd Symposium on Atmospheric Turbulence, Diffusion and Air Quality, Raleigh, NC, 19–22 Oct. 1976.

Husar R. B. and Patterson D. E. (1980) Regional scale air Pollution: sources and effects. *Ann. New York Acad. Sci.* **338**, 399–417.

Kadowaki S. (1976) Size distribution of atmospheric total aerosols, sulfate, ammonium and nitrate particulates in the Nagoya area. *Atmospheric Environment* **10**, 39–44.

Lavery T. F., Hidy G. M., Baskett R. L. and Mueller P. K. (1980) The formation and regional accumulation of sulfate concentrations in the northeastern United States. In: *Environmental and Climatic Impact of Coal Utilization*, (Edited by Singh J. J. and Deepak Adarsh), Academic Press, New York.

Lewis C. W. and Macias E. S. (1980) Composition of size-fractionated aerosol in Charleston, West Virginia. *Atmospheric Environment* **12**, 195–200.

Lippman M., Kleinman M. T., Bernstein D. M., Wolff G. T. and Leaderer B. P. (1979) Size-mass distributions of the New York summer aerosol. *Ann. New York Acad. Sci.* **322**, 29–44.

Loo B. W., Freuch W. R., Gatti R. C., Goulding F. S., Jaklevic J. M., Llacer J. and Thompson A. C. (1978) Large-scale measurement of particulate sulfur. *Atmospheric Environment* **12**, 759–771.

Lucero D. P. and Paljung J. W. (1974) Monitoring sulfur compounds by flame photometry. In *Instrumentation for Monitoring Air Quality*, ASTM Special Publ. 555. Philadelphia, PA.

National Research Council, Subcommittee on Ammonia (1979) *Ammonia*. University Park Press, Baltimore, MD.

Rodhe H. (1978) Budgets and turnover times of atmospheric sulfur compounds. *Atmospheric Environment* **12**, 671–680.

Stevens R. K., Dzubay T. G., Shaw R. W., Jr., McClenny W. A., Lewis C. W. and Wilson W. E. (1980) Characterization of the aerosol in the Great Smoky Mountains. *Envir. Sci. Technol.* **14**, 1491–1497.

Trijonis J., Eldon J., Gins J. and Berglund (1980) Analysis of the St. Louis RAMS Ambient Particulate Data. USEPA Report EPA-450/4-80-006a, Research Triangle Park, NC.

Waggoner A. P., Vanderpol A. H., Charlson R. J., Granat L., Trägårdh C. and Laisen C. (1976) The sulfate light scattering ratio. An index of the role of sulfur in tropospheric optics. *Nature* **261**, 120–122.

Winchester J. W. (1980) Sulfate formation in urban plumes. *Ann. New York Acad. Sci.* **338**, 297–308.

Wolff G. T., Monson P. R. and Ferman M. A. (1979) On the nature of the diurnal variation of sulfates at rural sites in the eastern United States. *Envir. Sci. Technol.* **13**, 1271–1276.